

## **Air/Sea Transfer of Gases and Aerosols**

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### **LONG-TERM GOALS**

Our long range goals for this project are to: 1) understand the effect of various physical and chemical properties of the air-sea interface on gas exchange, and 2) characterize the sea surface texture and turbulent boundary layers. These studies will provide a basis for future work on the active and passive sensing of the sea surface and the estimation of surface gas transfer velocities from such information. They will provide new insight into the mechanisms by which chemicals are transferred across the air/sea interface.

### **OBJECTIVES**

This project is part of a collaborative experimental study of gas exchange across the air/sea interface. Our objective for the final phase of the project was to demonstrate the capability to make a direct flux measurement across the sea surface using the eddy covariance technique. This would provide a measurement of flux with a time constant on the order of minutes, which would allow us to relate gas exchange rates to ocean surface texture, boundary layer turbulence, imposed surface wind stress, gustiness, and atmospheric stability. Simultaneous measurements of gas exchange and surface texture can ultimately provide the needed link between gas exchange rates and remotely sensed parameters, which will allow realistic estimates of the rates and variance of gas exchange across the air/sea interface.

### **APPROACH**

Our approach is to develop the capability to make eddy covariance flux measurements for a variety of chemical compounds with different physical and chemical characteristics. This requires making high resolution (~1 Hz) chemical measurements a few meters above the sea surface, simultaneously with the measurement of vertical winds. The use of eddy covariance for air/sea exchange studies has been limited by the availability of suitable chemical sensors. In this project, we designed and built an atmospheric pressure, chemical ionization, quadrupole mass spectrometer (referred to as API/CIMS).

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| 14. ABSTRACT<br><b>Our long range goals for this project are to: 1) understand the effect of various physical and chemical properties of the air-sea interface on gas exchange, and 2) characterize the sea surface texture and turbulent boundary layers. These studies will provide a basis for future work on the active and passive sensing of the sea surface and the estimation of surface gas transfer velocities from such information. They will provide new insight into the mechanisms by which chemicals are transferred across the air/sea interface.</b>   |                                    |                                     |  |   |                                    |
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This instrument is capable of low parts per trillion sensitivity for many gases at a time resolution of 1 Hz or better. This instrument was previously deployed in the RSMAS ASIST wind/wave facility. In this phase of the study, the instrument was deployed on Scripps pier in order to test its performance under real-world conditions. In this study, measurements were made for dimethylsulfide (DMS), a biogenically produced sulfur gas. Vertical wind measurements were made using sonic anemometry. In addition to the fast-response air measurements, the API/CIMS was used to measure the partial pressure of DMS in surface seawater. This was done by pumping surface seawater into the laboratory, equilibrating it with a nitrogen gas stream using a continuous flow membrane equilibrator.

## WORK COMPLETED

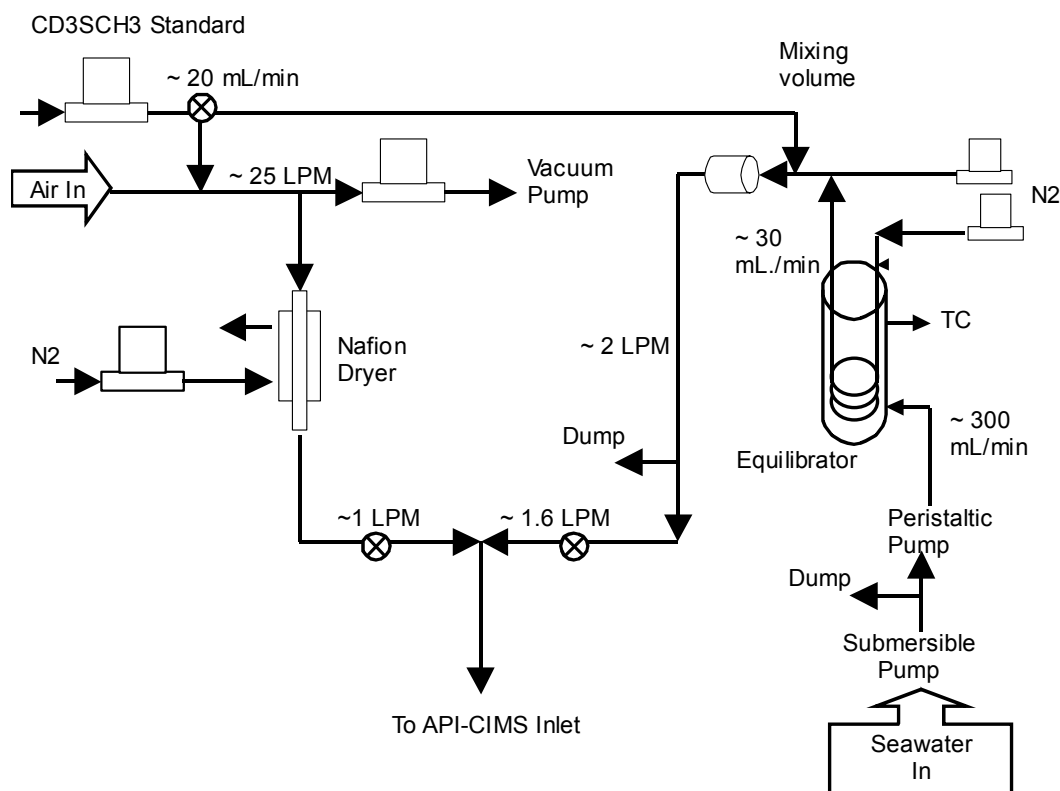
The Scripps pier deployment was carried out from January to March 2003. Preparation for this study involved the development of instrument control/datalogging software and electronics, installation of submersible pump, and modification of the Scripps pier lab to support the API/CIMS instrument. The effort involved testing various configurations of the instrumentation and assessing the frequency response and sensitivity of the instrument under field conditions. Analysis of the data resulting from the experiment is largely complete, and a manuscript describing the results is in preparation. This report contains a summary of preliminary results from this experiment.

## RESULTS

In this project, eddy covariance fluxes of DMS were measured using an atmospheric pressure chemical ionization mass spectrometer (API/CIMS) in positive ion mode. A similar approach has recently been used to measure DMS fluxes from aircraft (Bandy et al., 2002). The API/CIMS ion source consists of an atmospheric pressure flow tube in which air passes over a radioactive foil ( $\text{Ni-63}$ ). Ionization of DMS occurs via proton transfer from  $(\text{H}_2\text{O})_n\text{H}^+$ , where  $n=1,2,\dots$  to form  $(\text{CH}_3)_2\text{SH}^+$  ( $m/e=63$ ). The source is operated at high temperature ( $450^\circ\text{C}$ ) to minimize water clustering because the  $(\text{CH}_3)_2\text{SH}^+$  ion is unstable with respect to charge exchange with larger water clusters. For eddy covariance measurements, the air stream is dried using a Nafion membrane drier prior to entering the source. This improves sensitivity (by reducing water clusters) and eliminates the effect of variations in water vapor on instrument response. The ions are extracted into a differentially pumped quadrupole mass spectrometer which can be operated in either selected ion or scanning mode. The ions are detected using a pulse-counting ion multiplier and associated electronics. Data acquisition and control are performed by a National Instruments virtual device running on a real-time PXI computer. The user interface is a Visual Basic program operating in the Windows environment, which communicates via TCP-IP with the real-time computer. This instrument was constructed in our laboratory, using Extrel components, with a design similar to that of Eisele and Tanner (1993).

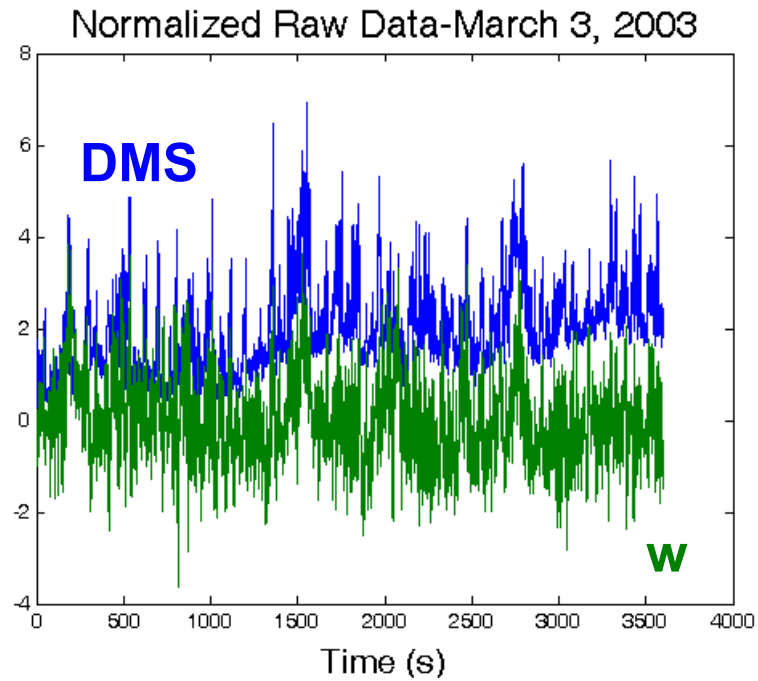
A stable isotope-labeled internal standard ( $\text{CD}_3\text{SCH}_3$ ) is used to calibrate the instrument during field operations. A small gas flow of internal standard is mixed with the analyte stream at the air intake and the masses of both the internal standard and the natural DMS are monitored by the mass spectrometer. This provides continuous, real-time calibration and allows for correction of drift due to minor changes in airflow rates, source temperatures, etc. Gas standards containing DMS and isotopically labeled DMS are produced in humidified high-pressure cylinders in our laboratory. These are calibrated against permeation tubes, which are in turn calibrated gravimetrically.

The API/CIMS was set up in the laboratory at the end of the Scripps pier. For atmospheric measurements, air was drawn to the inlet for analysis through ~130 ft of tubing from the boom at the western end of the pier. The boom housed the inlet and a Campbell CSAT sonic anemometer, which measured three dimensional wind speeds and direction, approximately 4 m above the sea surface. During the atmospheric analyses, the sonic anemometer collected data at 100 Hz and the API-CIMS collected data at 10 Hz. Ocean surface waters were analyzed for DMS for two minutes before and after each hour-long atmospheric analysis. Surface water (approximately 1 m depth) was continuously pumped to the lab by a submersible pump and, then, to a Teflon membrane equilibrator by a peristaltic pump. The equilibrated air was directed to the API/CIMS inlet for analysis (Figure 1).

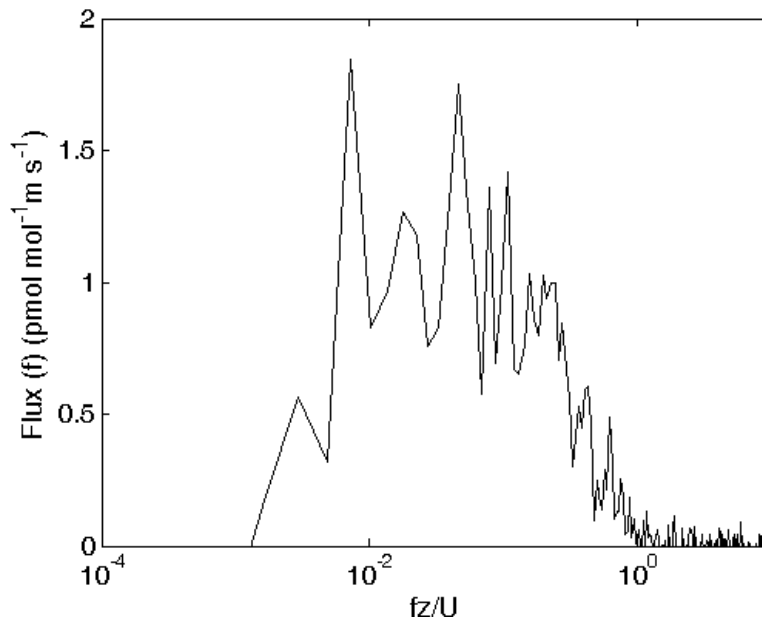


**Figure 1. Schematic of the analytical setup used to measure atmospheric and surface ocean levels of DMS off Scripps pier during this study. The atmospheric sampling inlet is to the left of the API/CIMS inlet and the seawater analysis inlet is to the right.**

Sixteen 1-hour flux records were acquired during the Scripps study. Because of the proximity of the site to the shore, data was acquired only during onshore airflow. Data acquisition was limited by low wind speeds, and the daily seabreeze cycle. An example of the data generated during this study is shown below in Figure 2. Correlation between the DMS and vertical wind records is present throughout the dataset. A cospectrum of DMS and vertical winds is shown in Figure 3. These data clearly demonstrate that the API/CIMS captured the flux due to turbulent motions in the atmosphere. On the high frequency end of the cospectrum, the flux vanishes around 1. This reflects the attenuation of high frequency fluctuations in the sampling tubing (Lenschow and Raupach, 1991; Massman, 1991).



**Figure 2.** An example of fast response DMS and vertical wind speed measurements ( $w$ ), taken 4 m above the sea surface at Scripps pier (March 3, 2003). The mean DMS level in air was 80 ppt, seawater DMS was 6.8 ppb, and the horizontal wind speed was  $2 \text{ m s}^{-1}$ . The data have means removed, and are normalized by their respective standard deviations.

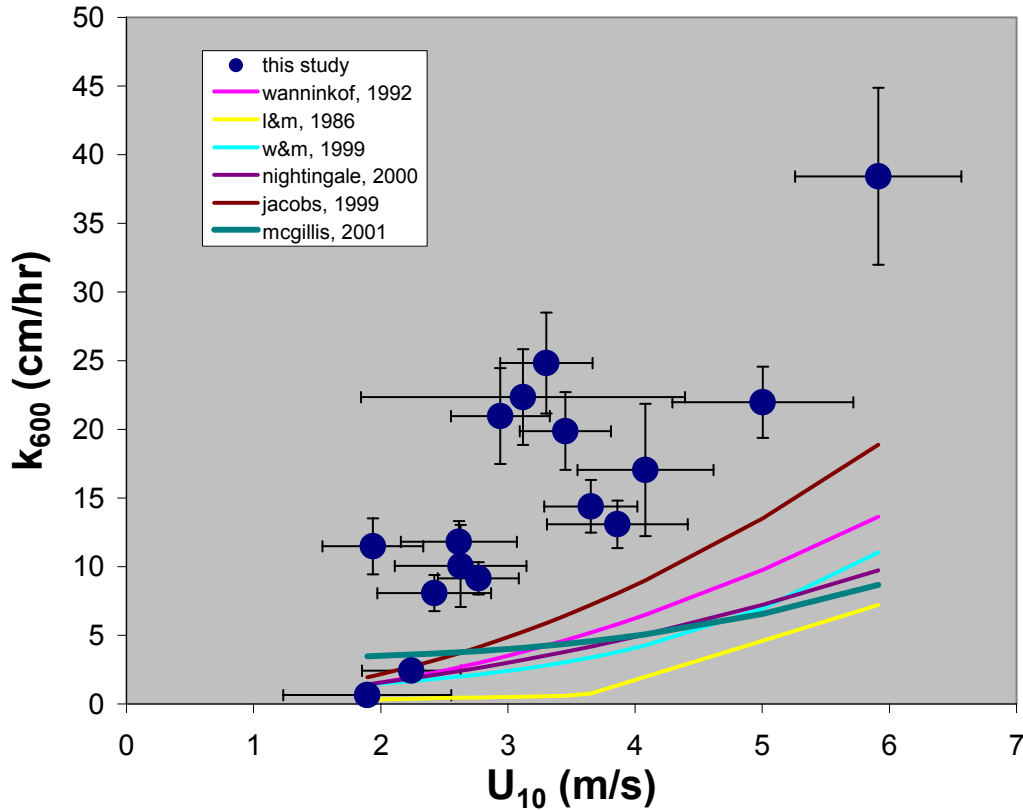


**Figure 3.** Cospectrum of DMS and vertical winds ( $w$ ) from the data set shown in Figure 2, plotted against normalized frequency.

Air/sea gas exchange is usually parameterized using the following expression:

$$F = k(\Delta C),$$

where  $F$  is the flux, and  $\Delta C$  represents the chemical concentration gradient of the emitted (or absorbed) compound between air and surface water. The gas transfer coefficient,  $k$ , or “piston velocity” is a proportionality constant between flux and concentration gradient, which encapsulates the physics of gas exchange. In this study, since the air/sea flux was directly measured and the concentrations in both the bulk air and surface ocean were measured, and the solubility is known, the gas transfer coefficient, can be computed directly from the equation above. Figure 4 is a plot of the gas transfer coefficient vs. mean horizontal wind speed for the results from this study. Also shown are a variety of other  $k$  vs wind speed parameterizations proposed for open ocean conditions. The  $k$  values determined for the range of wind speeds at Scripps are significantly higher than the open ocean parameterizations. These elevated gas exchange coefficients most likely reflect the additional turbulence at the site induced by wave/bottom interactions and by subsurface currents associated with the return flow from breaking waves onshore.



**Figure 6.** Gas transfer coefficient derived from direct flux measurements vs. horizontal wind speed. The data has been normalized to Schmidt number of 600 and the horizontal wind speed at 10 m above the surface. Also plotted are previous parameterizations of  $k$  vs. wind speed. Error bars represent the uncertainty ( $1\sigma$ ) of the DMS calibration (vertical), and the variance ( $1\sigma$ ) of the horizontal wind speed.

## IMPACT/APPLICATIONS

To our knowledge, this study is the first application of the API/CIMS technology to oceanography. We expect that it will find widespread use in real-time, fast response, highly sensitive detection of trace gases and other chemicals. We demonstrated that the instrument has the required sensitivity and time response to capture air/sea fluxes on short time scales. This capability will enable future progress on the difficult problem of understanding the physical processes controlling air/sea gas exchange. Such understanding will ultimately result in improved algorithms relating the state of the air/sea interface to remotely sensed properties.

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